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Delivery Order 0053: Multiscale Modeling Support

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Modeling Solutions, Inc.

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14. ABSTRACT <p>This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at Wright-Patterson AFB, Ohio. Multi-scale modeling was carried out to study mechanical, thermal and interfacial properties of multifunctional polymers for application in hybrids and composites. In order to establish competency in the new area of molecular modeling of composites and identify technical gaps in molecular modeling of organic polymer matrix composites the issue of developing core competency in computational materials science addressing the Air Force's need for developing next generation of polymer matrix composites, was addressed.</p> <p>Multiple research proposals were submitted. Along with atomistic and coarse-grained molecular dynamics (MD), mesoscale and lattice modeling were also used. Atomistic MD was used to study interfacial properties where as coarse-grained (bead-spring model) MD was used to obtain a general understanding of how network structure controls the mechanical properties of highly crosslinked polymers. The network formation of cross-linked polymers was studied using discrete lattice models. The mechanical properties of crosslinked thermoset molecules were studied using atomistic simulations. The understanding provided by this modeling effort shall be used towards guiding experiments in better designing these multifunctional hybrids.</p>								
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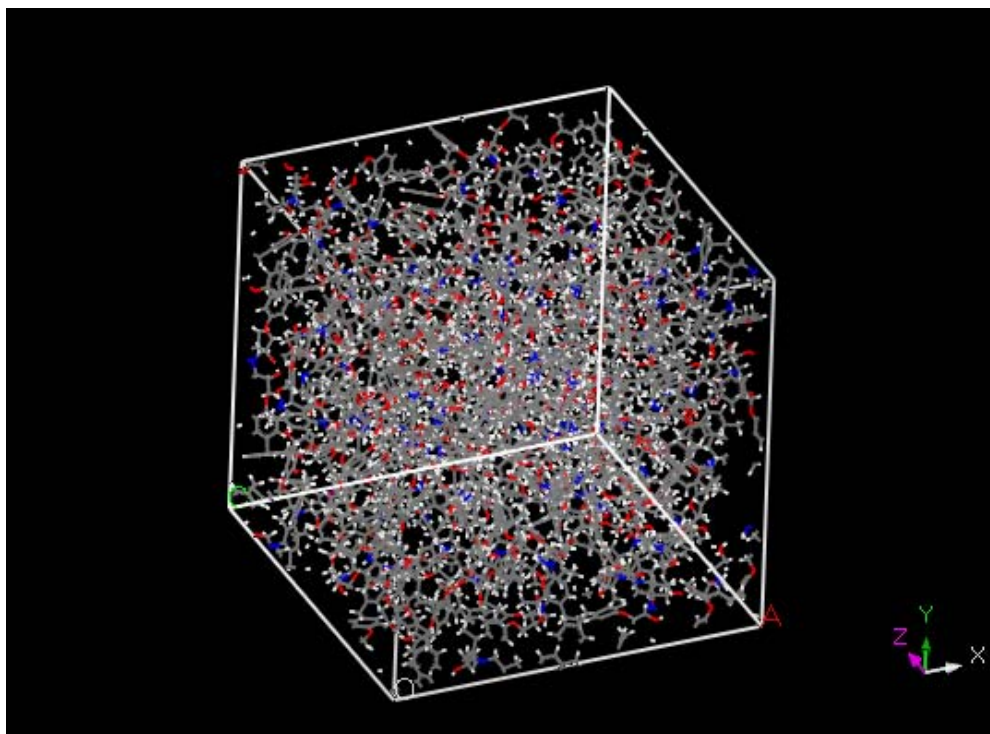
EXECUTIVE SUMMARY

Multi-scale modeling was carried out to study mechanical, thermal and interfacial properties of multifunctional polymers for application in hybrids and composites. In order to establish competency in the new area of molecular modeling of composites and identify technical gaps in molecular modeling of organic polymer matrix composites the issue of developing core competency in computational materials science addressing the Air Force's need for developing next generation of polymer matrix composites, was addressed. Multiple research proposals were submitted. Along with atomistic and coarse-grained molecular dynamics (MD), mesoscale and lattice modeling were also used. Atomistic MD was used to study interfacial properties where as coarse-grained (bead-spring model) MD was used to obtain a general understanding of how network structure controls the mechanical properties of highly crosslinked polymers. The network formation of cross-linked polymers was studied using discrete lattice models. The mechanical properties of crosslinked thermoset molecules were studied using atomistic simulations. The understanding provided by this modeling effort shall be used towards guiding experiments in better designing these multifunctional hybrids.

Keywords: Molecular Modeling, Molecular dynamics, Multiscale modeling, Mesoscale modeling, Lattice Models, Thermosets, Interfacial modeling

Section I: Description of Research

(1) Mechanical properties of Epon 862. Crosslinking of a model system consists of EPON-862 (Bis-phenol F/epichlorohydrin based epoxy resin) and EPI-Cure-W (diethyltoluenediamine, DETDA) was created. First of all, a stoichiometric mixture of EPON-862 and DETDA was build using Amorphous Cell module of Material Studio. The charges were assigned using group charge method build within Material Studio. The initial mixture contained 16 epoxy resin molecules and 8 curing agent molecules. Subsequently a 2 X 2 unit cell was created and the various groups were crosslinked. All simulations were performed using the Compass forcefield. The non-bonded van der Waals interactions were modeled as 12-6 LJ potential with a cutoff of 10 Å.



A body in equilibrium which is acted on by external forces balances it by internal stress which is a second rank tensor with nine components. In an atomistic simulation, the internal stress can be obtained using the virial expression. The application of stress to a body results in a change in the relative positions of particles within the body, expressed quantitatively via the strain tensor. In view of the fact that both the stress and strain tensors are symmetric, it is often convenient to simplify these expressions by making use of the Voigt vector notation. Note: the 6 x 6 stiffness matrix C is also symmetric, and hence a maximum of 21 coefficients are required to describe the stress-strain behavior of an arbitrary material fully. In addition, C is no longer a tensor, since it does not obey the required transformation rules. For an isotropic material, the stress-strain behavior can be fully described by specifying only two independent coefficients. To date, reported attempts to estimate the elastic moduli of amorphous polymers have adopted one of three approaches. We are using the static method to calculate the mechanical properties. In this approach, contributions originating from changes in configurational entropy on deformation,

and from the strain dependence of the vibrational frequencies is negligible and the elastic stiffness coefficients are calculated from numerical estimates of

$$d^2U/d\varepsilon_i d\varepsilon_j (=d\sigma_i/d\varepsilon_j).$$

Thus, having constructed an energy-minimized series of amorphous structures confined to a periodic cube, each structure is subjected to twelve deformations; three pairs in uniaxial tension/compression and three pairs involving pure shear, followed by a re-minimization to restore a state of detailed mechanical equilibrium. Each of these deformations corresponds to setting one of the components of the strain vector to some small value (for example $\varepsilon = 0.001$), while keeping all other components fixed at zero. The elastic stiffness coefficients can then be obtained by estimating the second derivatives of the deformation energy with respect to strain using a finite difference formula (for the diagonal components only), and by calculating $\Delta\sigma_i/\Delta\varepsilon_j$ for each of the six pairs of applied strains, where σ_i represents, in vector notation, elements of the stress tensor obtained analytically using the virial equation. For each configuration submitted for static elastic constants analysis, a total of 13 minimizations is performed. The first consists of a conjugate gradients minimization of the undeformed amorphous system. The target minimum derivative for this initial step is 0.1kcal/Å. However, to reduce the time required by the calculation, a maximum of 1000 steps will be performed in attempting to satisfy the convergence criterion. Following this initial stage, three tensile and three pure shear deformations of magnitude ± 0.0005 are applied to the minimized undeformed system, and the system is re-minimized following each deformation. The internal stress tensor is then obtained from the analytically-calculated virial, and used to obtain estimates of the six columns of the elastic stiffness coefficients matrix. At first the unit cell was minimized and the lattice parameters are as follows:

Length (Å) Angle (degrees)

A = 36.32900, alpha = 90.22810
B = 38.15030, beta = 87.85920
C = 40.49230, gamma = 85.93710

Elastic Constants (GPa)

23.09	1.263	-1.853	-3.47	-4.349	6.019
12.99	19.82	3.678	-0.9219	-2.356	3.01
8.476	5.37	-1.78	-4.921	-5.391	6.649
-0.2958	0.206	3.134	5.716	-3.18	0.007971
0.996	0.8999	5.066	3.822	-0.3984	-1.299
-1.912	-1.009	-1.665	-0.2207	-0.07238	3.621

Effective Isotropic Elastic Constants (GPa)

Tensile	:	11.05
Poisson's Ratio	:	0.2668
Bulk	:	7.894
Shear	:	4.360
Lame Const. Lamda	:	4.988
Lame Const. μ	:	4.360

These simulations are currently being refined to improve the values of the elastic constants.

(2) Ordering of liquid Squalane on a silicon dioxide surface: In collaboration with Prof Mesfin Tsige of Southern Illinois University at Carbondale.

Understanding the structure and thermodynamic properties of ultrathin films of low-molecular weight hydrocarbons adsorbed on solid surfaces is an area of fundamental and current interest with numerous technological implications [1-4]. The interfacial structure of liquid branched alkanes at solid surfaces has been a subject of several simulation and experimental studies. But, previous simulation studies are based on united-atom model in which each carbon and its attached hydrogens are treated as a single ‘atom’. To understand the structure and thermodynamics of branched hydrocarbons an all-atom description of the molecular structure, where the hydrogen atoms are treated explicitly, is required in order to capture, in principle, all of the required properties. An advantage of using an all-atom representation of the molecules rather than a united-atom lies in the ability to examine the role of molecular flexibility and internal vibrations affecting the molecular orientation in the system. Since the hydrogen atoms are treated explicitly in all-atom models, the requirement in terms of computer time is significantly larger than for united-atom models. Fortunately, the development of parallel MD algorithms and the availability of increased computational power have now reached the point where detailed atomistic simulation study of low molecular weight systems is possible.

The main objective of the present study is to elucidate the molecular basis for the structure of the liquid-solid interface of squalane. Squalane, $C_{30}H_{62}$, is a liquid hydrocarbon consisting of a C_{24} backbone with six symmetrically placed methyl groups as shown in Figure 1(a). Squalane is a natural moisturizer for the skin and is also used as a solvent for some nanocomposites, for example silica mixed with squalane is added to make-up products to make it soft, smooth, and powdery since the squalane is not a volatile solvent. It is thus important to understand the ordering of squalane on a solid surface.

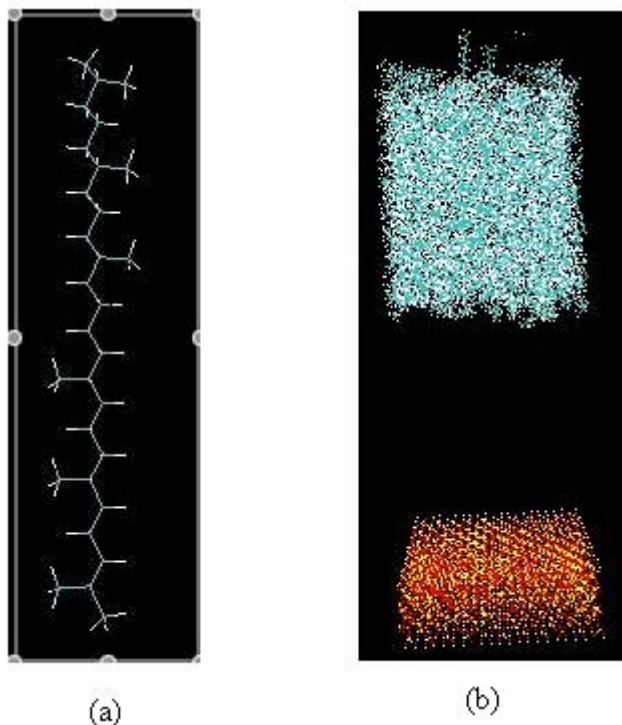


Figure 1. (a) structure of squalane projected on its carbon backbone plane and (b) snapshot of the starting configuration. The surface of the SiO_2 substrate is $54 \times 51 \text{ \AA}^2$ and the thickness is 20 \AA .

Molecular dynamics simulations of liquid squalane were performed at different temperatures (300, 325, 350, 375, 400, 450, and 500 K). The starting configuration for all the simulations is shown in figure 1(b). This initial configuration consists of 100 squalane molecules placed at a distance of 40 \AA from the hydroxylated SiO_2 surface. The Optimized Parameter for Liquid Simulation-All Atom (OPLS-AA) force field of Watkins and Jorgensen [5] was used in these simulations. All the simulations were performed in the NVT ensemble using the molecular dynamics code LAMMPS. Temperatures were regulated by a Nose-Hoover thermostat with a relaxation constant of 0.1 ps , and the simulations were run on average for about 10 ns .

Density profile of the liquid squalane in the direction perpendicular to the surface (z -direction) can deliver information about the structure of the liquid at the liquid/solid and liquid/vapor interfaces. It is important to note that none of the simulations showed any signs of molecules evaporating into the vacuum. Figure 2 shows density plots at different temperatures. The density profiles exhibit oscillatory patterns. As expected, the molecules organize in layers parallel to the surface diminishing with distance from the surface and the effect of the substrate can go as deep as 40 \AA into the liquid.

The first peak is weakly dependent on temperature while the rest of the peaks show strong temperature dependence, decreasing with increasing temperature. The distance between the peaks is about 5 \AA that corresponds to the size of the squalane molecule.

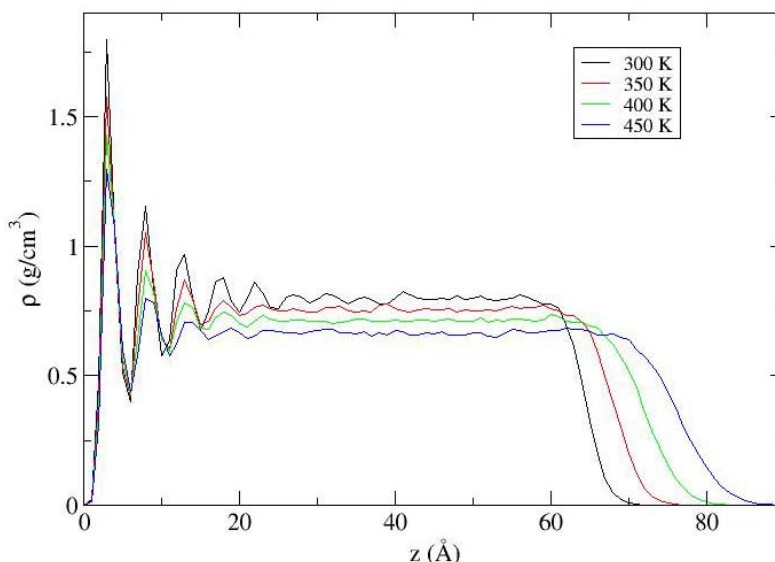


Figure 2. Density profiles for squalane at different temperatures.

Figure 3 shows 2-D snapshots of the first layer (corresponding to the first peak in Fig. 3) for three different temperatures. We clearly see that the squalane molecules at the liquid/solid interface are ‘lying down’ with their molecular axes parallel to the surface. The molecules are in trans conformations at 300 K but the molecules tend to bend at higher temperatures.

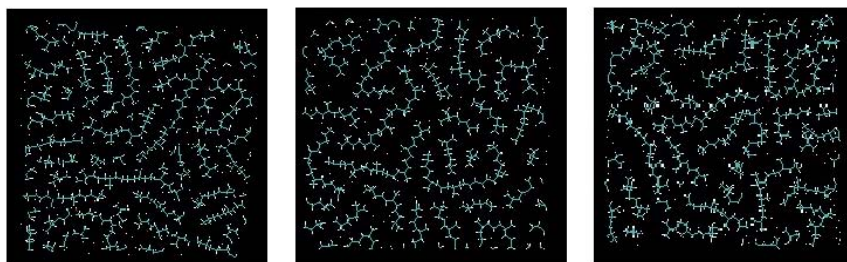


Figure 3. 2-D snapshots of the first layer at temperatures of 300, 400, and 500 K, respectively, from left to right.

In summary our simulation results clearly show that squalane forms layers near a hydroxylated SiO_2 surface with molecular axes parallel to the substrate. The effect of the substrate on the ordering of squalane near the interface depends on temperature. In addition orientation calculations for the chain back bone and the methyl group (CH_3), not reported here, show that the squalane molecules at the solid/liquid and liquid/vapor interface are lying down with their molecular axes preferentially parallel to the interfaces.

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(3) Monte Carlo simulation of thermoset modeling: A discrete approach: In collaboration with Prof Partha Biswas and Ras Pandey , University of Southern Mississippi.

Thermoset polymer system consists of epoxy group such EPON 862 and a cross-linking agent (such as diethylene toluene di-amine, DETDA) is studied via Monte Carlo simulation on simple cubic lattice models. The lattice approach provides only a coarse-grained description of structure and morphology of the generated network. The emphasis of our work here is on generic structural aspect of the network without taking into account the details of quantum chemical interactions. While the first-principles simulations are important in order to study the exact dynamics of the network, some of the basic structural properties are universal in nature and can be obtained from simple statistical model. These coarse-grained models retains the essential features of the network, which can be used as an input for constructing more realistic model all atom models.

The model used in our work is very similar Ising model applied to binary random alloy problem. The total energy of the model can be written as:

$$E = \sum_{i=1}^n \varepsilon_i + \sum_i \sum_{j:i < j} t_{ij}$$

where ε_i is the site energy for the species A or B and t_{ij} is the off-site (bonding) energy between the species i and j . The epoxy group (species A) and the cross-linker (species B) have functionality $f_a=2$ and $f_b=4$ respectively. Initially, A and B are randomly distributed in a cubic lattice of linear dimension L such that a lattice site cannot be occupied by more than one species. Network formation is started via bond formation between the species A and B provided that 1) A and B are non-bonded 2) each of them has a free degree of freedom or functionality to form a bond 3) they are nearest neighbors to each other. In this model, A can only be bonded to a maximum of 2 neighboring B species, whereas B can be bonded to a maximum of 4 neighbors of species A provided the rules 1 to 3 are satisfied. The network is then relaxed by choosing randomly species A or B using the metropolis algorithm. The lower energy moves are always accepted, whereas the higher energy moves are accepted with metropolis probability $P = \min [1, \exp(-\beta\Delta E)]$. The energy difference ΔE can be calculated by attempting to move a species A or B to an empty neighboring site and β is related to the inverse temperature $1/K_B T$. One such

energy lowering move is illustrated in Fig. 1. The parameters used in this calculation are $\varepsilon_{aa} = \varepsilon_{bb} = \varepsilon_{ab} = 0$ and $t_{ab} = 0.5$, $t_{aa} = 0.0$, $t_{bb} = 0.0$. The bond formation between A-A and B-B, have been neglected in this model, but can be included at higher temperature. Similarly site energies can also be chosen to include any chemical interaction between the species.

The results of our calculations are shown in Fig 2 and Fig 3 for cubic and square lattices respectively. In both the figures, we have plotted the maximum cluster size. In Fig 3, the results for a square lattice are presented. It is important to note that unlike in the cubic lattice, the size of the largest cluster in terms of the total volume of the system is reducing with increasing size. This suggests within this model, there exists no critical concentration of cross-linkers to form a connected network. This is however, not surprising in view of the fact that the degree of freedom for the species to move is 4 instead of 6. Once an isolated cluster is generated in this network, the system can not evolve to include this cluster in the spanning or infinite cluster. In summary, our preliminary calculation based on a simple lattice model in 3dimension indicates that there exists a critical concentration of the cross-linkers to form a spanning network of

infinite size. The cluster size distribution and other geometrical properties can be obtained for these model. Temperature dependence of the reaction rate can be taken into account by introducing an empirical reaction probability between A and B (which is unity at present) and that between A and A (which is zero in this model). In summary, our preliminary calculation based on a simple lattice model in 3dimension indicates that there exists a critical concentration of the cross-linkers to form a spanning network of infinite size. The cluster size distribution and other geometrical properties can be obtained for these model. Temperature dependence of the reaction rate can be taken into account by introducing an empirical reaction probability between A and B (which is unity at present) and that between A and A (which is zero in this model).

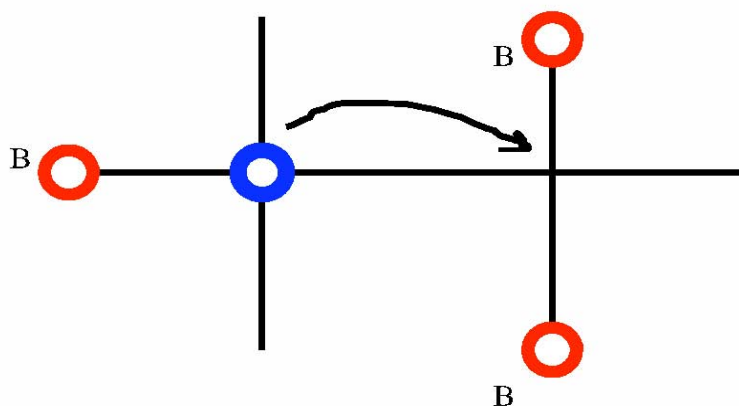


Fig. 1a

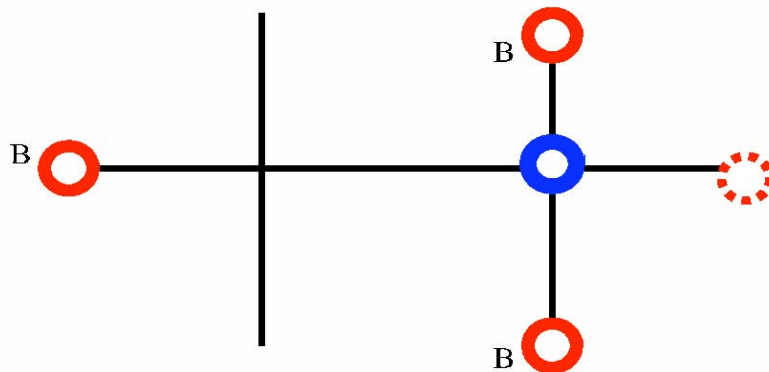


Fig 1b

Figure 1. A Monte Carlo move implemented in our work for relaxing the system. By moving the species A (in blue representing the epoxy group), the system lowers its energy. The initial and final energy of the model is respectively. Note that the species A (after moving) can no longer form a bond with the cross-linker (in red) indicated with a dotted line because of functionality requirement.

max cluster size as a function of Pb (square)

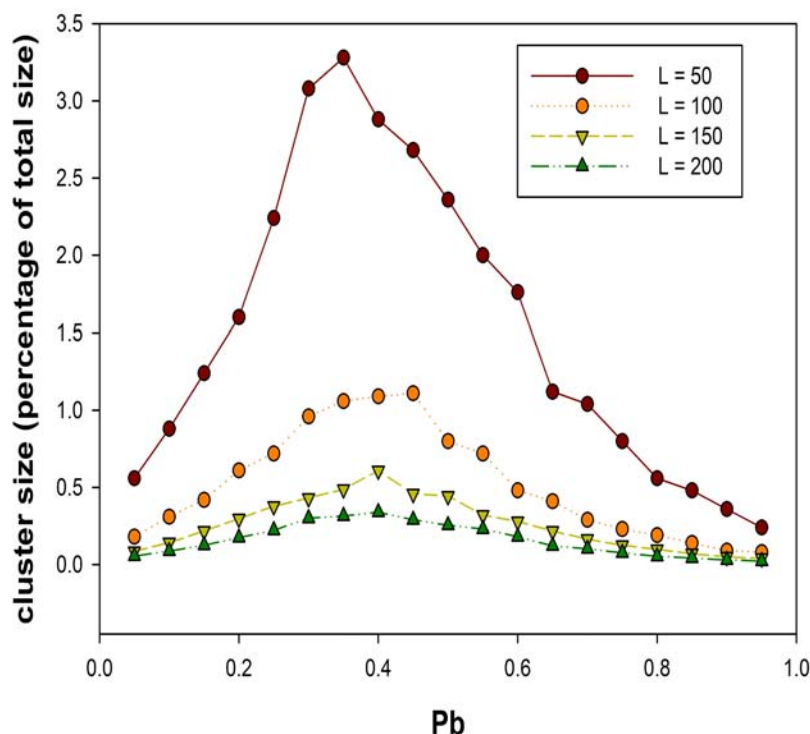


Figure 3. Maximum cluster sizes as a function of concentration of species B for a square lattice. The percentage of total number of species is plotted along y axis. Note that unlike in the cubic lattice, the volume of connected network is reducing with increasing system sizes. The numbers in the inset indicates the linear dimension of the model.

Section II: Research Proposals

Technical Principal Investigator and author of multiple research proposals seeking external funding for modeling efforts in RXBC.

(1) “Molecular Modeling of Interfacial Properties of Carbon Nanotube/Nanofiber Based Composites” by Soumya S. Patnaik, Ajit Roy, Jennifer Fielding and Katie Thorp, submitted to the Materials Directorate Computer Research Steering Group. This proposal received 50K funding.

Carbon nanotubes (CNTs)/nanofiber possess excellent combination of mechanical, thermal and electrical properties which has facilitated development of many multifunctional products. These exceptional properties of CNTs/nanofibers, has generated interest in their use in future aerospace structures. Research in AFRL/MLBC has shown CNT/nanofiber based nanocomposites to have good conductive properties. Currently, these are being explored as nanomaterials for reducing damage from lightning strike. Along with CNTs, nickel-nanostrands, and metal coated carbon nanofibers, have also been found to be very promising for use as reinforcing materials for nanocomposites that can be used as surface material for composites used in aerospace structures. Currently, statistical modeling of the composite structures is being carried out to determine effective electrical and mechanical properties.

However, a better understanding of several issues pertaining to alignment and dispersion of these nano-inclusions in various matrixes has to be achieved before these can really be used as nano-modified composites for aerospace applications. In order to achieve good electrical and mechanical properties, one of the critical components to be optimized is the interface strength between the matrix and the reinforcing nano-inclusion. There are conflicting observations in the existing literature regarding the nature of interfacial bonding in CNT/nanofiber-based composites. The nanometer length scale of CNTs/nanofiber renders experimental measurement of the interfacial strength extremely difficult, if not impossible. In summary, a molecular level understanding of the interfacial region is required, both to provide a fundamental understanding of the nature of the interface and also to help better adapt the statistical modeling by which the effective properties of the composites can be determined. The focus of this work will be to identify the key interface parameters to optimize the mechanical and the electrical properties of nano modified composites for lightning strike protection.

Proposed Research: We propose the interface modeling effort to be carried out in three stages.

1. **Molecular dynamics of crosslinked polymers:** Construction of molecular models of crosslinked polymeric materials is the first challenge that has to be undertaken in any molecular level modeling of thermosets. We propose to use MD to generate equilibrated atomistic models of resin/crosslinkers/solvent systems. In particular, three widely used structural epoxies, two bisphenol epoxies and a cyanate ester will be considered and in all cases diamine will be used as the curing agent. These epoxies have different mechanical properties and function over different temperature ranges. The curing process will be simulated by linking reactive sites within a certain cutoff distance. This method although not very rigorous can be improved upon by future work using MD coupled with kinetic MC. The network models created in this fashion will be studied for bulk properties such as shrinkage and transport of penetrants. Information regarding crosslinking density, degree of unreacted crosslinking sites and curing shrinkage is valuable for determining mechanical properties whereas barrier properties such as mobility of oxygen and water in the crosslinking systems are important to determine degradation of the resins. Results obtained from MD simulations will be compared with those using group contribution methods.

2. **Modeling of interfaces:** As a first step, the networks structures will be adsorbed onto various surfaces such as nickel and graphite. Molecular dynamics will be carried out to study interfacial adhesion and also to estimate the extent of the interfacial region.

3. **Large scale molecular dynamics simulation of nano-composites:** Large scale MD simulations which include nano-particle embedded in a resin matrix will be carried out using equilibrated resin network models generated in step 1 and incorporating our knowledge about the interface from step 2. Such a model can lay the basis of developing coarse grained models of these nanocomposite systems.

Impact: Currently, dielectric and mechanical properties of CNT and nickel-nanostrand based nanocomposites with different epoxies are being measured in-house. The proposed modeling can provide fundamental understanding of the various critical factors that are of importance while designing these materials. Also by guiding the modeling effort with the already available experimental data, we can generate realistic models for these nanocomposites; the tool can then be used to provide processing guidance in tailoring materials design of nanocomposites.

(2) Designing Resilin Based Elastomers - Proposals submitted to the ML Bio Program in collaboration with Katie Thorp, David Mollenhauer, Rajesh Naik and Matthew Dickerson. This proposal received \$80K funding:

Objective: To gain an understanding of structure-property relationship in resilin with an aim towards developing bio-derived and bio-inspired multifunctional hybrid composite materials that have unique mechanical properties. Previous research in resilin has been geared towards applications in drug delivery, MEMS devices (actuators) and medicine (synthetic vascular prostheses). Although exploratory in nature, we are proposing a collaborative modeling and experimental effort in developing these bio-elastomers for potential applications in sensors and as advanced aerospace materials. As the Air Force moves toward multifunctional, morphing structures our ability to expressly tailor the elastic properties of high-performance resins will become critical. The high deformation and resilience characteristics of resilin make it an ideal system to study as we begin to envision future morphing Air Force structures which may be expected to endure repeated exposure to large deformations while maintaining durability and predictable mechanical performance.

Introduction: Biological systems often use hierarchical structures to achieve unique property combinations. Through the study of these unique structures we can develop novel molecular approaches that are applicable to synthetic systems. Insect cuticle is a perfect biological archetype for nano-composites and presents great inspiration for developing materials with high strength and toughness [1]. The multifunctional nature of the cuticle requires an ability to exhibit a wide range of mechanical properties which are controlled by the composition and volume fraction of its constituents, primarily chitin fibers and resilin matrix [2], an unique elastomeric protein with remarkable mechanical properties [3]. With a resilience of 97% and an extremely long fatigue life, resilin is considered to be the most efficient elastic material known (in comparison, high resilience rubber is only 80% resilient with a much shorter fatigue life). Resilin therefore is an ideal model system to study and we see two important aspects to this. First, to learn how nature has optimized for a combination of resilience and durability and use this knowledge to help us design synthetic elastomers which could enable repeatable deformation in a morphing aircraft structure. Second, to use molecular tailorability to introduce multifunctionality in resilin-like elastomers, which would perhaps provide improvement from synthetic elastomers which lack hierarchical structures.

Unlike chitin which has been widely studied [2, 4, 5], the structure/property relationship of resilin, particularly the mechanism that gives rise to its elasticity, is not very well understood. To understand the elastic behavior of resilin, comparison has been made with other elastic proteins such as elastin, abductin and spider silks and several mechanisms that were previously used for elastin have been proposed [6]. The first and simplest mechanism proposed is based on rubber elasticity in which resilin is considered as a network of random chains consisting of Gaussian distribution of end-to-end chain lengths between cross-links. On application of stress, the conformational freedom of chains is restricted and is distorted from the most probable distribution, thereby reducing the entropy. This decrease in entropy provides the restoring force to the original state. Urry and coworkers [7] although agreeing that the restoring force is entropic in nature, proposed an alternate model in which the elasticity arises from the protein's β -spiral structure. On stretching, the conformational freedom of the β -spiral is restrained and this loss of entropy provides the restoring force. Both of these proposed ideal models only consider the contribution of entropy to the elastomeric forces but do not take into account any

effect of the internal energy. We believe that the internal energy contribution has a significant role in the elasticity of resilin, due to the fact that resilin exhibits high resilience only when swollen with polar solvents such as water [8].

To date, the detailed characterization of resilin has been hampered by the small amount of protein produced by insects and the crosslinked protein's insoluble nature. The opportunity to investigate this unique protein has recently emerged through the identification of a putative resilin gene, GC15920, in *Drosophila melanogaster* [3]. The theoretical product of CG15920 (referred to here after simply as resilin) is a 603 amino acid protein possessing three domains: a 62 residue central core, a 324 residue long N-terminal domain, and a 217 residue long C-terminal region [3]. While the N- and C- terminal domains of resilin are dominated by multiple copies of a 15- or 13- residue motif, respectively, the central core of the protein has been characterized as possessing significant similarity to chitin-binding proteins. Based on primary structure similarities to other elastic proteins, resilin has been suggested to fold into a series of β -turns, resulting in a β -spiral structure. Unfortunately, experimental evidence has not yet been gathered to support this supposition [3].

Description of work: In order to develop an understanding of the role of structure in controlling the mechanical properties of resilin, we propose a collaborative multi-prong approach which includes the modeling of structure and mechanical properties, as well as the production and mechanical characterization of this protein. The initial research effort will be divided into two tasks, the first of which will focus on the modeling of protein structure, calculating and measuring mechanical properties. The second task will be devoted to recombinant production and characterization of resilin. Although we will initially study the model protein, rec1-resilin, which is based upon the N-terminal domain consensus repeat of resilin [9], additional WT structures may also be analyzed. Beyond protein structure, the effects of crosslinking (forming di- and tri- tyrosine crosslinks) and water content on materials properties will also be evaluated. The proposed studies are expected to provide insight into the superior elastic behavior of resilin compared to synthetic elastomers thus advancing our fundamental understanding of the differences between synthetic elastomers (where the elastomeric force is mainly entropic in nature) and bio-elastomers such as resilin (where both entropic and internal energy contributions compete). Furthermore, by proposing a complimentary modeling and experimental effort we hope to be able to design elastomers with multifunctionality which can be tailored for different applications.

The second aim of this study is to assess the feasibility of fabricating resilin-based multifunctional nanocomposites. In place of chitin, we will attempt to produce resilin/carbon nanotube (CNT) composites. The incorporation of CNTs into elastomers such as natural rubber has been previously demonstrated to positively impact the mechanical, electrical conductivity, heat conductivity, and electromagnetic shielding properties of these materials [10]. It has also been previously established that elastomeric materials filled with conducting particles at a level near the percolation threshold experience drastic changes in electrical resistance when subjected to mechanical or chemical deformation [10]. The exploration of this phenomenon for elastomeric materials filled with CNTs has been scarcely reported on and the literature is totally lacking in examples of such phenomena in protein-based materials. Dependent upon the success of developing resilin/CNT nanocomposites, the development and performance of resilin/CNT-based sensors and will be investigated.

Modeling and Mechanical Characterization: The initial part of the modeling effort will be towards structure determination with special emphasis on the putative elastic repeat sequences GYSGGRPGGQDLG and GGRPSDYGAPGGGN [6] and homology modeling will be carried out to model the protein structure. Preliminary homology studies [11] based on sequence comparison methods generated structures with very few β -sheets and almost no β -turns. A more detailed homology study that looks at other elastic proteins will be undertaken and the predicted models will be subsequently refined by results from the experimental characterization. Such a combined approach will help us identify the validity of the earlier proposed β -spiral model for resilin. Once a robust 3D structure is determined, molecular dynamics will be carried out to calculate the mechanical properties and also to identify the elastic regions of the protein. Such a study will help us isolate the internal energy contribution to elasticity for resilin and perhaps provide insight into the structural motif required for high resilience. The repetitive segments in resilin are not hydrophobic but hydrophilic in nature thus expecting to show significant interaction with the solvent. Different crosslinking sites will be identified and modeled. The effect of both the crosslinking density and water content on mechanical properties will be calculated. This will be further validated by strain-field measurements using three dimensional digital image-correlation technique for samples with different cross-linking density and moisture content. Apart from providing a fundamental understanding of the elastic mechanism being exhibited, the present study will help guide the synthesis of these bioelastomers with tailorable properties. The various sub-tasks can be identified as follows:

- i. Homology modeling of protein structure
- ii. Mechanical properties by molecular dynamics
- iii. Strain-field measurements using three dimensional digital imaging technique

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- (3) Modeling of Nanoscale Assembly Tools in collaboration with Timothy Bunning.
This proposal received funding for a shared postdoctoral position.

We propose a multiscale modeling approach focused on mesoscale models to study long range order development in nanostructured organic/inorganic hybrid materials that address fundamental aspects of the approaches outlined in Task 1 and 2. Spatial inhomogeneities that range from a few nanometers to microns and exhibit dynamical phenomena on time scales of micro-to-milliseconds are important to understanding structure development. Problems at such length and time scales cannot be fully addressed using atomistic or continuum methods. Therefore, mesoscale methods that encompass computational techniques at the intermediate scale are desirable. By modeling materials using fundamental units that are between the molecular and the continuum scale, we should be able to provide fundamental insight into the development of ordered arrays from otherwise disordered systems. The research will focus largely on the two important aspects of morphology development: (1) Transport behavior of multi-component systems that can lead to “top-down” structure development as in photo-driven holographic patterning or reconfiguration as in nanoparticles triggered adaptive materials and (2) Nanoscale assembly processes within spatially defined regions as in block co-polymers or fluidic cavities. In order to address the specific nature of these two problems, we propose using two distinct mesoscale methods: Mesodyn [1] – a density based method; and Dissipative particle dynamics (DPD) [2] – a particle based method. It is expected that the different morphologies developed from these mesoscale studies will be incorporated in subsequent combined studies with molecular dynamics to calculate verifiable material attributes such as mechanical or electrical properties.

Transport behavior of multi-component polymeric systems: These polydispersed systems exhibit spatially heterogeneous dynamics with large variation in concentration of the constituent components accompanied with a change in morphology. We plan to use Mesodyn [1] in which the component density fields (which are defined at discrete grid points) driven by chemical potential gradient and Langevin noise, dynamically evolve towards the free energy minimum. By using the Kohn-sham equivalence scheme in which an out-of-equilibrium system can be represented by an equilibrium system with external constraints, the component density fields can

be represented as function of densities of the ideal system and a non-ideal potential reflecting non-equilibrium interactions.

Assembly of nanoscale systems: The equilibrium thermodynamics of molecular self-assembly processes is characterized by a balance between the competing effects of energy minimization and thermal fluctuations and can be described by minimizing Gibbs free energy. At certain temperature ranges, the entropic contribution to the free energy has the most significant influence on the self-assembly process and has to be accounted for along with the contribution from the potential energy. We plan to use DPD [2], a recently developed molecular dynamics technique originally used for simulating complex fluids but more recently applied to polymeric systems (off-lattice Flory-Huggins model). Mesoscopic particles are used to represent clusters of molecules and in addition to conservative forces, stochastic drive and dissipation are introduced to represent internal degrees of freedom. Compared to traditional MD, longer time steps can be used and hydrodynamics is better preserved than other mesoscale methods such as Brownian Dynamics. Groot and Madden [2] found that a better representation of the hydrodynamics modes responsible for large-scale collective motions of polymers to be the essential ingredient in correctly predicting the morphologies of different systems. This also provides a more robust way of understanding the complex pathway by which each system micro-phase separate.

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(4) Proposals submitted to the 2007 Lab Director's Fund:

(a) Title: Multi-Scale Bridging in Polymeric Material Systems by Soumya S. Patnaik, Greg Schoeppner and A. Kelkar and R. Mohan, Dept of Mechanical Engineering, North Carolina A&T State University, Greensboro, NC 27411.

Introduction: With the ever increasing use of fiber reinforced organic composites in aerospace applications, computational fracture mechanics of polymers has come to play a key role in light weight composite materials development. Computational techniques that can bridge the molecular level interactions with the continuum level behavior are necessary to address material deformation behavior such as crack initiation and propagation which are based on phenomena that takes place at an exceedingly faster rate at the molecular length and time scales, and a relatively slower rate at the continuum length scale. Computational techniques that bridge across the different length and time scales (example: MAAD: macroscopic, atomistic, ab-initio dynamics; EAM: embedded atom method), have focused primarily on single molecule metallic material systems. This multi-scale bridging gets further complicated in polymeric material systems. Unlike in conventional fracture mechanics where the fracture is usually assumed to propagate in an ideally brittle material and crack propagation takes place by breaking individual bonds at the crack tip (Figure 1) [1], in the case of polymers, crack propagation occurs by breaking or pulling polymer chains and effective multi-scale techniques that rely on energy continuity and preservation across the different length and time scales are required.

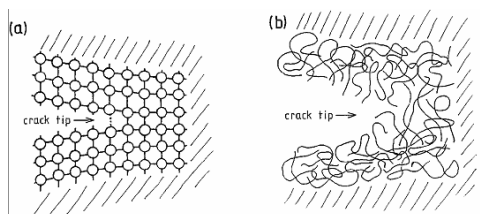


Figure 1. A crack in (a) a brittle atomic crystal, e.g., silicon, and (b) polymer.

Description of proposed work: We propose extending current multiscale modeling approaches that have been applied in metallic and crystalline systems towards multi-molecular polymeric material systems. Two different coupling schemes between mesoscale models for the polymers and finite element models will be investigated. (a) Literature indicates that quasi-continuum method [2] is essentially an adaptive FE method with the atomistic to continuum link achieved via Cauchy-Born rule [3]. The Cauchy-Born rule assumes that the continuum energy density can be computed using an atomistic potential, with a link to continuum via deformation gradient. This results in selective representation of atomic degrees of freedom. Instead of treating all atoms making up the system, a small relevant subset of atoms is selected to represent, by appropriate weighting, the energies of the system as a whole. Based on their kinematic environment, the energies of individual “representative atoms” are computed either in non-local fashion corresponding to the straight forward atomistic methodology, or within a local approximation based on continuum model. This representation results in a computational model with varying density with more atoms sampled in highly deformed regions (such as near crack tip, defect cores) and correspondingly few atoms in less deformation regions further away. This configuration is adaptively updated as the deformation evolves. (b) Another coupling atomistic and finite element model methodology cited in the literature treats the atomistic model (analogous to polymer particle dynamics models) as a discrete system and is used to couple the atomic model to the continuum model in metallic structures [4]. This method permits analysis of a relatively large size of the domain in conjunction with accurate representation of the atomistic behavior that is not obtainable with a continuum model. An atomistic model is employed in the regions where atomistic physical behavioral interactions are predominant. This atomistic domain is coupled with continuum domain via an intermediate domain where both atoms and finite element meshes overlap each other and is called the interface domain for coupling. The atoms in the interface domain are called embedded atoms. A solution procedure with staggered solutions between the atomistic domain and continuum finite element domain is employed.

The applicability of these two types of approaches for polymeric material configurations using dissipative particle dynamic descriptors and appropriate linking rules will be investigated. A phased approach that include both sequential and fully coupled strategies for coupling the length scales will be considered. Initial activities will focus on fundamental investigations based on mesoscale and continuum mechanics models, their bridging and evaluation of their applicability employing analogous approaches as briefly described earlier.

Relevance of work to ML: MLBC has a long term interest in optimizing mechanical properties of fiber reinforced organic matrix composites for aerospace applications. Although multiscale modeling is essential in order to predict thermo-mechanical properties of advanced aerospace composites, our modeling effort so far have focused mainly on studying micro scale failure. Very recently, we have also started an effort in molecular modeling of composites. By

developing methodology that can link both atomistic and finite element methods this project will help transition our molecular modeling effort into engineering design.

Project Impact: Failure prediction of polymer and polymer matrix composite has historically been rooted in continuum based approaches borrowed from the failure criteria and fracture mechanics based approaches originally developed for metallics. The absence of a widely accepted failure modeling approach for polymer and polymer composites in concert with the experimental observations has compelled research to examination of these materials at smaller and smaller scales to understand fundamental material behavior. However, the ability to relate the molecular level scale behavior back to the continuum level performance is still absent. Till date, almost all the significant multiscale modeling efforts in composites are being carried out at the micro-to macro level. By providing molecular level understanding and coupling with finite element methods, this will be a small fundamental step towards predicting strength and toughness of polymeric material systems based on their molecular description.

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(b) Title -Modeling of Thermal Conductivity in Nano-modified Organic Matrix Composites, Soumya Patnaik & Joni Arnold.

Improvement in thermal/electrical conductivity in polymers is essential for designing new organic matrix composites. Although this has been achieved to certain extent by nanomodification of the polymeric matrix, a more thorough understanding is required to enable materials scientists to substantially improve these properties. Inclusion of small concentration of carbon nanotubes or single graphene sheet into polymer matrix has shown promising results. Studies on electrical conductivity of CNT-polymer nanocomposites revealed low concentration (such as 1-2%) of CNT is enough to percolate through polymer matrix to observe transition to an electrically conducting phase. For electrical conductivity, percolation threshold is the only significant quantity for the insulator-conductor transition. However for thermal conductivity, such criteria are yet to be established. The order (orientational order) may have drastic effects on the thermal transport efficiency of polymer nanocomposites. We propose to investigate the concentration, nanostructure, orientational order effects on the thermal transport properties of CNT-polymer and graphene-polymer nanocomposites using fundamental molecular theories and molecular dynamics simulations. The modeling effort will be complimented by experimental measurements. This study will enhance our understanding of thermal transport through model systems and will help developing guiding principles for designing new polymer nanocomposites with tailored transport properties.

© Title – Nanoparticle Inductive Heating for Shape Memory Polymer Activation, Soumya Patnaik, Jeff Baur, Ryan Justice, Dave Justice & Gabe Jacobson

Abstract: Material systems such as shape memory composites can be reconfigured to enable multi-mission vehicles such as the Morphing Unmanned Air Vehicle. Triggering is typically done with resistive heating which requires intricate integration of wire heaters ultimately limiting the range of deformation. The use of magnetic nanoparticles that can be inductively heated offers the potential to achieve quicker and more uniform non-contact heating that does not limit the range of deformation. However, many of the details about the impact of nanoparticle morphology, thermal environment and mechanical deformations are still not fully understood. We propose a complimentary modeling and experimental effort to elucidate the fundamental mechanism of this novel activation scheme. Using a combination of ab-initio and molecular dynamics methods to characterize the magnetic hysteresis, calculate anisotropic energy effects and develop interaction potentials, we intend to investigate heat transfer from nanoparticles to polymer at the molecular level. Simultaneously, experiments will be carried out to support the model and understand the effect of nanoparticle morphology (clustering), composition and aspect ratio, on thermal transport. This information should provide a “quick look” as to whether inductive heating of nanoparticles is the most promising and flexible method for activation of shape memory composites.

(5) Laboratory Research Initiation (LRIR) submitted to AFOSR Program Manager: Dr. Charles Y-C Lee, AFOSR/NL, Task Manager: Dr. Katie Thorp,

Title: Advancing multifunctional composites through molecular modeling.

1.0 Summary: We propose molecular level modeling of structure-property relationships in cross-linked (thermosetting) polymers. Although, thermosetting resins have found great applicability in high performance composites, the development of most resin systems has been purely ad-hoc or based loosely on experimentally-derived theories. A more complete understanding of the association between the resin properties and its molecular nature will enable us to introduce true multi-functionality. Advanced aerospace applications in polymer matrix composites (PMC), adaptive materials and thermal management all demand the development of such multifunctional resins which are tailored and optimized for specific applications. We thus propose both development of molecular modeling tools for cross-linked polymers and then applying these tools to study different classes of resins with the ultimate goal of being able to design new resins. A new 6.1 effort in this area will bring advances in academic research in molecular modeling to cross-linked polymers and use computational material science tools to further the development and understanding of PMCs. A close tie between this new modeling effort with the already existing experimental in-house efforts in high temperature PMCs, processing science, durability and thermal management will provide validation of the modeling efforts thus creating a unique platform for resin development. Modeling of thermosetting resins at this comprehensive scale has never been successfully accomplished before and this work will revolutionize the approach of PMC development and insertion.

1.1 Motivation and Rationale: The intent of this effort is to develop the approaches necessary to allow for design of new resin systems from the beginning with a focus on improving the property or properties that are desired (i.e. thermal stability, toughness, hydrolytic stability, conductivity). In addition, through the use of molecular modeling approaches a greater breadth of potential resin chemistries should eventually be screenable than those that can be tried by wet chemistry approaches. The use of these molecular models should also allow for fundamental understanding of cure processes and degradation mechanisms which will allow for more rapid

insertion and improved applicability to those transition applications that are most appropriate for the expected system failure mechanism.

From the early part of 1970's through today, a substantial amount of work has been done by NASA and the Air Force to develop new, higher-temperature resin systems that would work in composite applications such as engine front frames, stators, and exhaust-washed structures [1]. Through the 1990's the entire development work was focused on empirically-based resin development focused around modifications to backbone and endcap chemistry in an attempt to improve thermal oxidative stability and processability [2]. Although some significant advances were made (such as the inclusion of Phenylethynyl endcaps and hexafluoro-imide backbones) a fundamental understanding of the relative benefits of different backbone or endcap chemistry was never generated. In addition, a full understanding of the cure processes and chemical kinetics is still unknown.

Early during the development of advanced polyimide chemistries, the industry settled into the use of norbornene-terminated resin chemistries. These systems demonstrated some improved thermal stability over other endcap approaches and quickly became included in several commercially-available systems [1]. Unfortunately, it was not until after about 20 years of widespread use that the hydrolytic instability of the norbornene endcap came to light [3]. This instability resulted in significant degradation of resin properties when exposed to moisture for even limited amounts of time [4]. In addition, the norbornene endcap proved to have some variability during processing that affected the hydrolytic stability and led to confusion during several experimental programs that were attempting to address the source of the hydrolytic stability problem [5].

Once the limitations of the norbornene chemistries were identified (although still not fully understood) the industry quickly moved to demonstrate Phenylethynyl endcap systems which did not appear to suffer from the same hydrolytic stability problems. A new resin system was developed at AFRL/MLBC utilizing this new "better" endcap [6]. The system was termed AFR-PE-4 and after \$20M of investment from the JSF JPO and others it has been demonstrated to a TRL of 6 for engine applications. Unfortunately, no fundamental work has been done to understand the cure reactions, process kinetics, or degradation mechanisms. As a result, additional investments by ManTech and others are still being made in AFR-PE-4 in an attempt to better understand the cure processes to reduce cost and cycle time during production. In addition, without a fundamental understanding of the potential degradation mechanisms, an appropriate focus on transitions is limited by the huge amount of testing necessary to investigate every potential weak-link of the system.

This empirical approach to resin development has led to a significant amount of duplication of work across the research community, as well as significant amounts of efforts being devoted to non-optimized resin chemistries. In today's research environment with limited funding availability, this empirical approach to new system development is not practical and significantly limits the potential for future developments in resins for high-performance polymer composites. In addition, the empirical approach does not give a full understanding of the cure processes or system degradation mechanisms or kinetics which might become a problem later in use.

1.2 Research Objectives and Scientific Questions: The primary objective of the proposed research is to model multifunctional aerospace thermosetting polymers at the molecular level

with an aim to design and optimize/tailor specific mechanical, thermal, electrical and degradation properties. Such a bottom-up approach which links the resin properties with its molecular structure is a crucial step in our efforts to discover, validate and prototype the next generation of advanced light weight load-bearing composites with thermal and radiation protection capabilities. Our ultimate goal of designing organic matrix composites for specific properties requires a multiscale hierarchical approach which relies on linking computation methods that address different length and time scales. Such an approach which couples first principle methods and molecular dynamics (MD) at the atomistic level, large scale MD and coarse-grained MD at the nano-scale, mesoscopic particle-based and field-theoretic models at the submicron scale and finite element continuum modeling at the macroscopic level is better suited to model the bulk properties of these advanced composites which can be considered to have three basic components – the polymeric matrix or resin (with or without nano reinforcement), fiber and fiber/resin interface. Although the size scale of an engineering composite structure requires the use of continuum methods, a fundamental understanding of the material structure property relationships can only be derived from molecular based methods. Similarly, the study of the matrix/fiber interface requires an atomistic approach. The use of molecular models becomes even more significant in multifunctional resins which ideally need to be tailored for additional properties without sacrificing their original/intrinsic properties.

Presently as a first step, our focus in this proposed research is to develop atomistic level understanding of the structure/property relationships in thermoset polymers. The more long term goal is to interface the atomistic models with coarse grained and finite element models (for example, see 1.5.1). Although atomistic molecular dynamics (MD) [7-11] has been widely used for the study of synthetic polymers, these studies have been mainly limited to thermoplastics and elastomers. So far, the bulk of computer simulations studies of thermosets available in the literature are mainly at the coarse-grain level, either bond fluctuation based Monte Carlo simulations [12] or bead-spring model based MD simulations [13-15]. While generating useful insight into the dependence of the physical properties of thermosetting polymers on their cross-link networks, these studies have not been able to provide structure-property relationships and specific correlation with the chemical structure of the resin system. Recently few MD based articles [16-17] have appeared in the literature but a comprehensive study which provides fundamental understanding of structure-property relationships is still lacking.

To achieve our objectives we will address such scientific questions as:

- i) How can you model realistic cross-linked polymers at the molecular level?
- ii) What are the various properties of interest that can be calculated from molecular modeling?
- iii) How is the structure of the resin monomer, temperature of curing, cross-linked density and crosslinked functionality related to the mechanical and transport properties of the thermoset?
- iv) What changes can be made in the choice of monomer, cross-linker and processing conditions to attain desirable properties?

1.2 Proposed Research: There are two significant parts of the proposed research. Of particular interest is development of suitable tools that can accurately model and characterize thermoset resins at the molecular level. In the second part these tools will be utilized to study

structure property relationships and degradation mechanisms in multifunctional thermosetting polymers. Special emphasis will be on studying the effect of crosslinking density and degree of curing along with the chemical functionality on mechanical properties and transport phenomena. Initially we will focus on epoxy-amine cured systems typical of polymer materials used as matrices for aerospace grade carbon fiber-based composites. Subsequent studies will extend to other classes of thermosetting polymers including polyimides, cyanate esters and bismaleimides. Although the primary method used will be MD, Quantum mechanics (QM) and Lattice simulations will also be supplemented as needed. The development of in-house molecular modeling capabilities will avail the DOD High performance computing resources and also be closely associated with experimental work for validation of the modeling approaches.

1.4 Description: 1.4.1 Method Development: One of the major barriers in conducting atomistic simulations of thermosets is the lack of protocols for building highly cross-linked polymeric networks based on specific reaction conditions and chemistry of resins and cross-linkers. Examples of existing capabilities include various approaches, some based on molecular dynamics simulations that build up a network on-the-fly, with others based on taking an equilibrated polymer melt, which is examined for proximity of groups capable of reacting prior to bond formation and re-equilibration [18,19]. Aspects of chemistry of actual thermoset formation, such as loss of small molecules following crosslink formation are not usually supported and the existing methods too easily generate defects such as highly strained local regions. Development of methodologies to generate equilibrated atomistic models of highly cross-linked networks based on reactant structures and reaction kinetics of thermoset resins allowing for subsequent molecular dynamics study is therefore necessary. Along with generating a starting description of the molecular network, efficient ways of generating equilibration structures is also required. Apart from combining Monte Carlo and MD distance criteria methodologies to build atomistic cross-linked epoxy networks, methods based on discrete lattice models which can capture underlying thermodynamics and reaction kinetics at the same time providing relaxed unstrained local regions will also be explored (see 1.5.2). The protocol and algorithms developed are expected to be transitioned into user friendly thermoset molecular builder via collaboration with industry and software development companies (see 1.5.3). Advances in analysis tools is also required that analyze molecular dynamics results and cater specifically to composite matrix property calculations such as material elastic constants (primarily stiffness and compliance constants), density and coefficient of thermal expansion. Since the next order goal is to link the atomistic modeling with higher level mesoscale modeling, analysis tools to calculate parameters for coarse grained/mesoscale models from molecular dynamics is also desirable.

1.4.2 Structure/property relationships: In order to develop and optimize true multifunctional thermoset resins, we need a better understanding of the development of the cross-linked structure which is a function of the reaction kinetics of the resin monomer and crosslinker and the diffusion rates of the polymerizing components. A study that simultaneous takes into account both the kinetic of the reaction rates and the diffusion rates is required to estimate their relative contributions and provide information about the extent of curing. Once the crosslinked structure is known a detailed study of the dependence of the various properties of interest on the structure can be carried out.

We propose a two phase study that at first looks at the cross linked structure formation and then the dependence of material properties on chemical constituents and the degree of curing

and flexibility of the backbone. Although the reaction kinetics of epoxy based resins is very well understood, those for thermosets based on polyimides, cyanate esters and bismaleimides is not. We propose to combine the use of QM and Reactive MD calculations to determine the reaction rates of these resin and crosslink systems and also to see the effect of temperature, concentration and degree of polymerization. This knowledge will be used in Lattice simulations to develop a better understanding of the global network formation. Various crosslinkers and resin monomers systems will be studied. The bulk properties of the crosslinked network structures thus formed with varying crosslinking functionality, backbone flexibility and degree of curing will be explored using MD, to develop structure/property relationships. Atomistic modeling of an epoxy based thermoset is currently being carried out (see 1.5.4) focusing on thermal conductivity calculations. Mechanical properties of coarse grained network structure is also being carried out for some simple ideal systems (see 1.5.5). Along with thermal and mechanical properties, we are also interested in degradation properties which are will be studied using QM and Reactive MD. Such a study will facilitate the molecular modeling study of high performance resin systems both with and without nano-modification and will be a valuable tool in characterizing composites for aerospace applications.

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Co-Investigator of the following proposals.

(1) AFOSR BAA (Broad Agency Announcement): Discovery Challenge Thrusts topic Thermal Transport Phenomena and Scaling Laws, August 2007 – “Interfacial design of polymer nanocomposites with enhanced thermo-mechanical properties” - Pawel Keblinski (RPI), Soumya Patnaik, David Cahill (Univ. of Urbana Champaign) & Tia Benson Tolle.

(2) ML CMSE, June 2007 – “Discovery and Improvement for Energy Harvesting, Storage and Power Generation” - Douglas Dudis, Alan Yeates, John Ferguson, William Mitchel, Soumya Patnaik & John Maguire.

(3) Joint Proposal with Industry (Boeing and Accelrys, Inc) – “Developing tools for atomistic modeling of thermosets”. This led to the formation of a Special Interest Group for Simulations of Advanced Composite Polymers by Accelrys, Inc.

(4) High Performance Computer Modernization Program 2007 Joint Opportunities for Minorities (JEOM) program. This was a joint program with Rome Labs. Received funding for a summer Masters Student

Section III: Additional Duties

- (1) Technical Supervision of Dr. Vikas Varshaney, Research Scientist, UTC.
- (2) Technical Supervision of Mark Kujawski, student.
- (3) POC for Modeling of Nanocomposites for the Minority Leader’s Program, a congressional interest item program.

Section IV: Publication

- (1) Molecular Dynamics Study of Thermal Conductivity of Curing Agent-W (Detda), Vikas Varshney, Soumya S. Patnaik, Barry Farmer & Ajit Roy, Proceedings of the SAMPE Technical Conference, 2007.
- (2) Heat Transport in Epoxy Networks: A molecular dynamics study, Vikas Varshney, Soumya S. Patnaik, Barry Farmer and Ajit Roy, in preparation.

Presentation:

(1) Presented poster titled “Molecular Modeling of Network Polymers” to the RX Scientific Advisory Board, 24th October, 2007.

(2) Presented talk titled “Multiscale modeling of Polymer Matrix Composites” at the AFRL Advanced Composite Branch and AFOSR Polymer Matrix Composite Program review (7-10 August, 2007).

(3) Challenges in Modeling Multifunctional Organic Matrix Nano-composites for Advanced Aerospace Applications, Soumya S. Patnaik, Invited talk at Workshop on Challenges in Computer Simulations, Bridging the time and length scales, July 2007, Singapore.

(4) Presented a talk on “Multiscale Modeling” at the In house review on October 4th, 2006.

Miscellaneous:

(1) Organized symposium “Computational Materials Science” on October 30 & 31, 2007 in the SAMPE Fall Technical Conference held in Cincinnati, Ohio.

(2) Received travel grant for 2007 APS Professional Skill Development Program.